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Biogenic Volatile Organic Compound (BVOC) Emissions from Various Endemic Tree Species in Turkey

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ABSTRACT

Compositions of biogenic volatile organic compound (BVOC) emissions from seven endemic tree species (Troy Fir, Uludag Fir, Cilician Fir, Oriental Sweetgum, Boz Pirnal Oak, Ispir Oak and Vulcanic Oak) in Turkey were determined. Field samplings were carried out in the forested areas using a specific dynamic enclosure system during the summers of 2011 and 2012. The selected branches of tree species were enclosed in a chamber consisted of a transparent Nalofan bag. The air-flows were sampled from both inlet and outlet of the chamber by Tenax-filled sorbent tubes in the presence of sunlight. Isoprene, monoterpenes, sesquiterpenes, oxygenated sesquiterpenes and other oxygenated compounds including sixty five BVOC species were analyzed with a GC/MS system. Temperature, humidity, photosynthetically active radiation (PAR) and CO_2 concentrations were monitored both inside the enclosure and in ambient air. Calculated emission rates were normalized to standard conditions (1000 μmol/m^2 s PAR and 30°C temperature). Ispir Oak, Oriental Sweetgum and Cilician Fir were the highest BVOC emitters with total normalized emission rates of 19.4 ± 19.2, 16.3 ± 16.1 and 15.5 ± 11.4 μg/g/h, respectively while Boz Pirnal Oak had the lowest emission rate of 0.84 ± 0.68 μg/g/h. Alpha-pinene, beta-pinene, beta-myrcene and limonene were the compounds dominating the monoterpene emission profiles while trans-caryophyllene, isolongifolene, alpha-humulene and copaene were the prominent sesquiterpenes. Predominant oxygenated compounds were also found as eucalyptol, linalool-L and alpha-terpineol. As reported in the literature, coniferous and broad-leaved species were predominantly monoterpene and isoprene emitters, respectively. Oxygenated compounds were the third most prominent BVOC group and sesquiterpenes had relatively lower contributions for all species.

Keywords: BVOC emissions; Dynamic enclosure system; Endemic tree; Turkey.

INTRODUCTION

Vegetation covering the landmasses releases several biogenic volatile organic compounds (BVOCs). BVOCs including terpenes (isoprene, monoterpenes and sesquiterpenes) and oxygenated compounds (alcohols, aldehydes, ketones, acetates) are important for atmospheric chemistry since they contribute to secondary organic aerosol formation and play an important role in the oxidative capacity of the atmosphere (Andreae and Crutzen, 1997; Fuentes *et al.*, 2000; Niinemets *et al.*, 2011; Sun *et al.*, 2012). Furthermore, because of their high reactivities, BVOCs affect the chemical composition of the atmosphere as they photochemically react with nitrogen oxides (NO_x) and form tropospheric ozone (Fehsenfeld, 1992; Roselle, 1994; Simpson, 1995; Bonn and Moortgat, 2003; Fares *et al.*, 2011).

BVOC emissions are mostly sampled by leaf/needle or branch enclosure measurements for the plant species either in laboratory or on-site (Komenda *et al.*, 2002; Padhy and Varshney, 2005; Dominguez-Taylor *et al.*, 2007; Ortega and Helmig, 2008; Joo *et al.*, 2010; Fares *et al.*, 2011; Matsunaga *et al.*, 2011; Baghi *et al.*, 2012; Matsunaga *et al.*, 2013). In these studies, BVOC emission compositions of numerous plant species including common and several site-specific (endemic) species were determined, and the attention was generally focused on trees as the most substantial component of vegetation (Owen *et al.*, 1997; Tambunan *et al.*, 2006; Räisänen *et al.*, 2009; Fares *et al.*, 2011).

In order to understand biochemical emission mechanisms and related controlling factors in detail, long-term and one or a few species based studies can be more reasonable

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(Harley *et al.*, 1996; Kempf *et al.*, 1996; Boissard *et al.*, 2001). Stone pine (*Pinus pinea*) and Scots pine (*Pinus sylvestris l.*) are two common trees that were frequently investigated for their seasonal and diurnal BVOC emission patterns in several studies (Staudt *et al.*, 1997; Street *et al.*, 1997; Sabillon and Cremades, 2001, Komenda and Koppmann, 2002; Räisänen *et al.*, 2009). Several tree species were also included in some studies to determine their species-specific emission rates (Owen *et al.*, 1997; Padhy and Varshney, 2005; Calfapietra *et al.*, 2009). For example, Geron *et al.* (2001) investigated 18 American oak (*Quercus*) species and 6 species from other genera. In Japan, Tambunan *et al.* (2006) also determined isoprene emissions of 42 indigenous species.

Getting knowledge on vegetative emissions of endemic species (that do not naturally grow in any other region) in a selected region may be important to provide information on local air composition. Japanese Cedar (*Cryptomeria japonica*) and Bamboo-leaf Oak (*Quercus myrsinaefolia*) were studied for their monoterpene and isoprene emissions by (Bao *et al.*, 2008; Matsunaga *et al.*, 2011; Matsunaga *et al.*, 2012b; Matsunaga *et al.*, 2013). Three endemic Mexican trees; Sacred Fir (*Abies religiosa*), Netleaf Oak (*Quercus rugosa née*) and Patula Pine (*Pinus patula*) were also investigated for their isoprene and monoterpene emissions by Dominguez-Taylor *et al.* (2007) to guide the future biogenic emission inventories for the Mexico City area. However, there is only one study in the literature that directly focused on BVOC emissions from forested areas in Turkey (Aydin *et al.*, 2014). The objective of this study was to determine the normalized BVOC emission rates (at 1000 μmol/m^2 s PAR and 30°C temperature) of isoprene, monoterpenes, sesquiterpenes, oxygenated sesquiterpenes and oxygenated compounds from seven endemic tree species in Turkey. Seven tree species, i.e., Troy Fir (*Abies nordmanniana* subsp. *equi-trojani*), Uludag Fir (*Abies nordmanniana* subsp. *bornmuelleriana*), Cilician Fir (*Abies cilicica* subsp. *isaurica*), Oriental Sweetgum (*Liquidambar orientalis*), Boz Pirnal Oak (*Quercus aucheri*), Ispir Oak (*Quercus macranthera* subsp. *syspirensis*), Vulcanic Oak (*Quercus vulcanica*), were investigated by conducting on-site measurement campaigns in different regions.

MATERIALS AND METHODS

Sampling Program

On-site samplings were conducted in the natural habitats of seven tree species between June 2011–August 2012. Three middle-aged (20–40 years) and healthy (i.e., no pest or aphid affected, having well-developed stem and branches, not obstructed by neighboring plants, favorable soil conditions and no other biotic/abiotic stress sources) trees were selected for sampling. BVOC samples were collected concurrently from two different branches of three selected trees of each species. Thus, BVOC emission rates of each species were calculated by averaging six values (3 trees × 2 branches). Measurements were conducted during photosynthesis of trees in the presence of sunlight (generally between 10:00 a.m.–14:00 p.m.) in summer months. All sampled trees were selected in open parts of the forest canopy to avoid underestimation of emissions due to the shaded leaves during the samplings. The collected samples were kept at 4°C until they were analyzed in the laboratory. Table 1 illustrates the sampling program including the studied species, sampling regions, sampling dates, and environmental conditions during the samplings. The sampling sites are also shown in Fig. 1.

Seven endemic tree species consisting of three coniferous and four broad-leaved trees were investigated. Turkey has four of the forty fir species known in the world which covers 2136 km^2 land area as pure fir forestlands, and three of these (Troy Fir, Cilician Fir, Uludag Fir) are among the endemics investigated in this study (GDF, 2010). The four broad-leaved species included three oaks and a sweetgum species. Oriental Sweetgum (or Turkish Sweetgum) is a rare endemic tree such that has a narrow distribution only about 5 km^2, additionally it has a special oiled secretion (balsam or sweetgum oil) that is used as a medicinal product like the other sweetgum species (Celik *et al.*, 1997; GDF, 2010). Oak (*Quercus*) species have the largest natural reserve in Turkey's forestland inventory including 18 species, 9 subspecies, 2 varieties and 7 natural hybrids (GDF, 2004).

Sampling Method

A specific dynamic branch enclosure system was used for sampling of BVOC emissions. Selected healthy branches of the trees were enclosed into transparent Nalofan bags (~7 L). The air-flows were sampled from both inlet and outlet of the enclosure by Tenax-filled adsorbent sorbent tubes. Nalofan bags have been commonly used for air sampling due to their inertness. Some recent applications using Nalofan bag as a chamber include the sampling of odorous gas emissions (Dincer *et al.*, 2006), volatile organic compounds (VOCs) emissions from an apple tree (Vallat *et al.*, 2005), a fig tree (Grison-Pige *et al.*, 2001), moss roses (Caisard *et al.*, 2006), and maize (Hoballah *et al.*, 2004). Temperature, humidity, CO_2 and PAR (photosynthetically active radiation) were continuously monitored and recorded both in the enclosure and in ambient air. Conditions in the enclosure were regulated to provide similar conditions to ambient air. Air circulation inside the enclosure was provided by consistent air inflow and outflows via two Teflon tubes connected to diaphragm pumps. The inflow air was purified by passing through three sequential columns containing silica gel, potassium iodide (KI) and activated carbon to remove humidity, ozone, and VOCs in ambient air, respectively. The operational scheme of the measurement system was given in Fig. 2. Both purified inflow and BVOC contained outflow rates were regulated by automatic mass flow controllers (MFCs) (Aalborg DFC26) at 5.83 L/min and 0.15 L/min, respectively. There were also two other Teflon tubes placed in the enclosure for by-passing the excess air and supplying air to the CO_2 analyzer at a flow-rate of 1 L/h. In order to avoid greenhouse effect in the enclosure under sunlight, cold water was circulated by a spiral Teflon tubing inside the bag using a circulating water bath. The integrated single humidity/temperature probe was also placed inside the chamber using a small cone-shaped case to protect the probe

Table 1. Details of the sampling program.

Species	Binomial Name (Latin)	Sampling Date	Region	Coordinates (UTM)	Averaged Environmental Parameters During the Samplings							
					Ambient air				Inside the enclosure chamber			
					T (°C)	RH (%)	PAR (μmol/m^2 s)	CO_2 (ppm)	T (°C)	RH (%)	PAR (μmol/m^2 s)	CO_2 (ppm)
Troy Fir	*Abies nordmanniana* subsp. *equi-trojani*	08–10 July 2011	Kalkim/ Canakkale	(35N) 510030, 4395705	24.8	45.7	1756	367	34.7	32.1	1580	425
Boz Pirnal Oak	*Quercus aucheri*	23–25 July 2011	Bodrum/ Mugla	(35N) 538885, 4105584	35.7	29.6	1707	370	42.3	34.1	1536	376
Oriental Sweetgum	*Liquidambar orientalis*	27–29 July 2011	Koycegiz/ Mugla	(35N) 652300, 4085250	34.8	46.1	1747	369	43.7	36.3	1573	287
Cilician Fir	*Abies cilicica* subsp. *isaurica*	09–11 Sep. 2011	Mut/ Mersin	(36N) 547660, 4070820	24.4	34	1691	367	30.4	11.2	1522	339
Uludag Fir	*Abies nordmanniana* subsp. *bornmuelleriana*	20–22 June 2012	Aladag/ Bolu	(36N) 381554, 4497233	22.7	45	1894	397	31.6	25.6	1705	378
Ispir Oak	*Quercus macranthera* subsp. *syspirensis*	18–20 July 2012	Mudurnu/ Bolu	(36T) 353189, 4494034	26.6	51.1	1502	389	30.1	35.8	1352	268
Vulcanic Oak	*Quercus vulcanica*	06–08 Aug. 2012	Egirdir/ Isparta	(36S) 309013, 4178771	26.3	38.6	1073	401	30.2	33.9	965	275

from direct sunlight. PAR sensor (Li-Cor LI-190 Quantum Sensor) has to be leveled horizontally to make accurate measurements. Since it was not possible to place the sensor inside the chamber in this way, PAR was monitored only outside the chamber. An experiment was conducted to determine the PAR attenuation inside the bag. One of the two identical PAR sensors was placed into a blank enclosure chamber while the second one outside the chamber. PAR values were monitored concurrently and recorded in one minute intervals for several hours covering a wide range of solar angles. During this experiment, average PAR values outside and inside the chamber were 1145 ± 158 and 1037 ± 137 μmol/m^2 s, respectively. Average attenuation rate of the bag was determined as 10 ± 2% and no systematic difference was observed with the varying solar angle. Based on this experimental extinction rate, the PAR values in the chamber were determined by multiplying those measured outside by a correction factor of 0.90.

Installation of the enclosure chamber was the most critical operation of the sampling that should be achieved without any damage/disturbance to branches and leaves since this may cause overestimated emissions. For the first two hours of the experiment, enclosure system was purged with purified ambient air to provide steady-state environmental conditions and to stabilize the emissions from possible initial disturbances during installation of the chamber. The purge time was selected as 2 h based on a recent study indicating that emissions are stabilized within this period (Oz, 2012). Following the purging, the air was sampled simultaneously from both the inlet and outlet lines for an hour. Tenax TA filled sorbent tubes were used to adsorb BVOCs from the enclosure. Enclosed branches were harvested at the end of the samplings to determine the dry foliage weight and leaf area. Dry foliage weight was obtained by drying the sample in an oven at 60°C for 48 hours while total leaf area was measured with a portable leaf area meter (Li-Cor LI-3000C). Using these data, both dry foliage weight and leaf area based emission rates were calculated.

Laboratory Analysis

Samples were analyzed for 65 compounds (isoprene, 21 monoterpenes, 15 sequiterpenes, 3 oxygenated sesquiterpenes, and 25 oxygenated VOCs) with a gas chromatograph (GC) (Agilent 6890N, Agilent) equipped with a mass selective detector (Agilent 5973 inert MSD, Agilent) and a thermal desorber (Tekmar, Aerotrap 6000). Samples were desorbed for 10 min at 240°C using helium flow at the rate of 40 mL/min. Internal trap temperature during sample desorption was kept at 35°C. The trap was desorbed for 1 min at 240°C. Then, it was baked for 10 min at 250°C. Valve oven and transfer line temperature of the thermal desorber was 200°C.

The chromatographic column was HP5-MS (30 m, 0.25 mm, 0.25 μm) and the carrier gas was helium at 1 mL/min flowrate and 37 cm/s linear velocity. The split ratio was 1:40. The inlet temperature was 240°C. Temperature program for VOCs was: initial oven temperature 40°C, hold 3 min, 40°C to 120°C at 5 °C/min, hold 5 min, 120°C to 240°C at 30 °C/min, hold 3 min. Ionization mode of the MS was electron impact (EI). Ion source, quadrupole, and GC/MSD

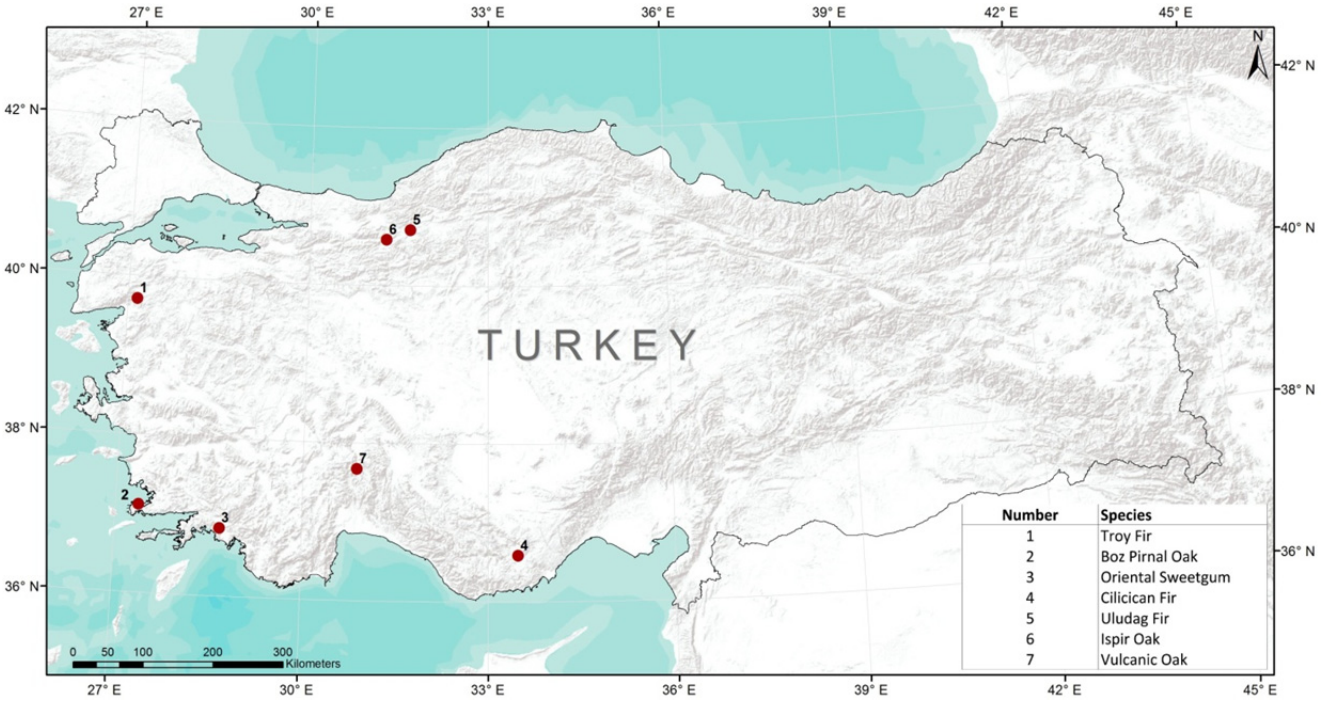

Fig. 1. Sampling sites.

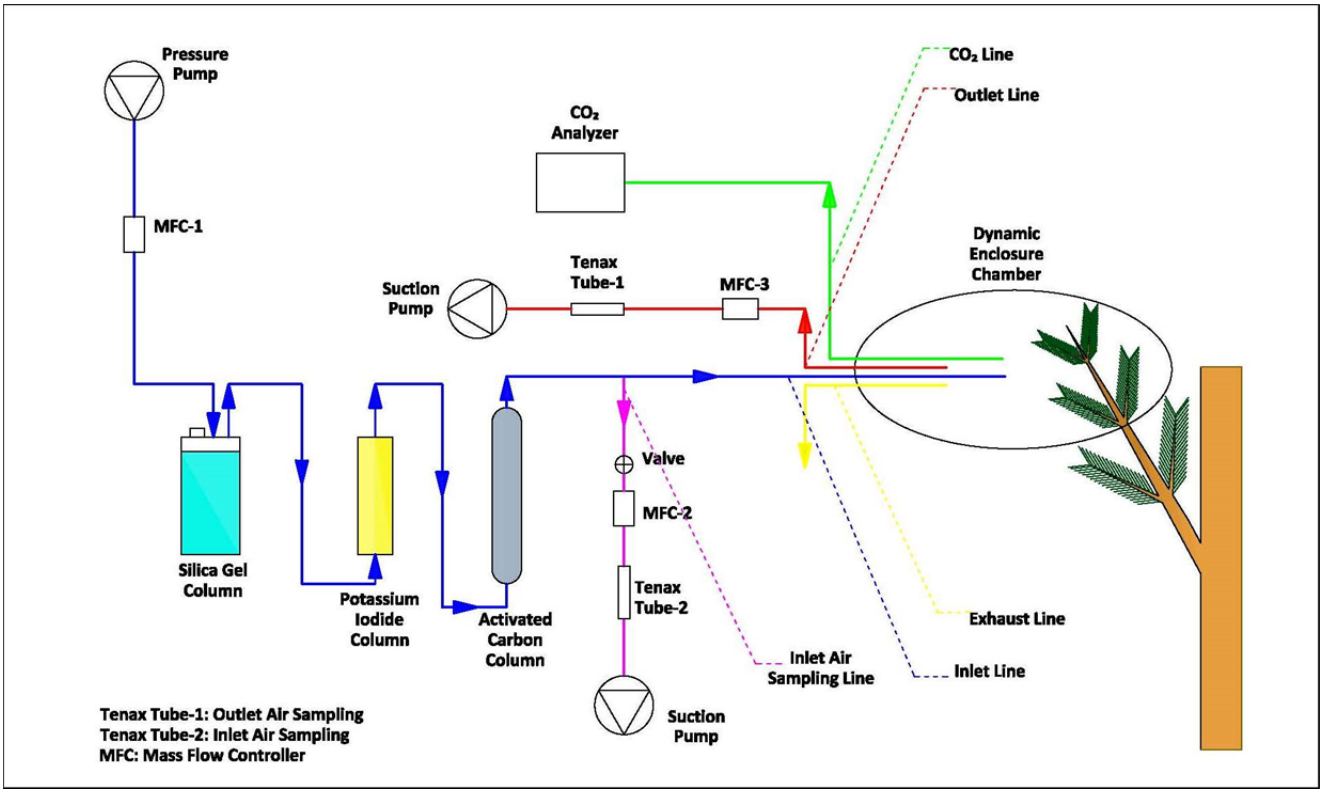

Fig. 2. Operational scheme of the measurement system.

interface temperatures were 230, 150, and 280°C, respectively. GC/MS was operated at "scan" and "selected ion monitoring" modes simultaneously. Compounds were identified based on their retention times (within ± 0.05 minutes of the retention time of calibration standard), target and qualifier ions and were quantified using the external standard calibration procedure. Calibration standards in methanol including 65 compounds (isoprene, 21 monoterpenes, 15 sequiterpenes, 3 oxygenated sesquiterpenes, and 25 oxygenated VOCs, see also Table 2) were obtained from SPEX CertiPrep, UK.

Table 2. Normalized BVOC emission rates (average ± standard deviation) for the species (µg/g/h) at standard conditions (at 1000 µmol/m^2 s and 30°C).

Group	Compound	Troy Fir	Boz Pirnal Oak	Oriental Sweetgum	Cilician Fir	Uludag Fir	Ispir Oak	Vulcanic Oak
Isoprene	Isoprene	1.34 ± 1.11	0.028 ± 0.026	15 ± 15.2	14.1 ± 10.5	1.5 ± 1.39	19.2 ± 19	9.79 ± 7.57
MT	Tricyclene	0.0045 ± 0.0042	0.00045 ± 0.0007	0.00012 ± 0.000044	0.00046 ± 0.0002	0.0015 ± 0.00097	0.00046 ± 0.0004	0.00026 ± 0.0003
MT	Alpha-Pinene	0.17 ± 0.068	0.013 ± 0.0003	0.042 ± 0.04	0.4 ± 0.31	1.42 ± 0.94	0.016 ± 0.02	0.013 ± 0.01
MT	Alpha-Fenchene	0.0027 ± 0.0028	0.00017 ± 0.000066	0.00014 ± 0.000028	0.00043 ± 0.00023	0.00049 ± 0.00022	n.d.	n.d.
MT	Camphene	0.035 ± 0.019	0.00058 ± 0.00051	0.0016 ± 0.0016	0.0025 ± 0.0016	0.022 ± 0.012	0.0017 ± 0.0012	0.0012 ± 0.0011
MT	Sabinene	0.014 ± 0.011	0.0016 ± 0.0015	1.1 ± 0.69	0.0063 ± 0.0042	0.048 ± 0.0095	0.0069 ± 0.0076	0.014 ± 0.015
MT	Beta-Pinene	0.47 ± 0.49	0.023 ± 0.022	0.049 ± 0.047	0.4 ± 0.38	0.34 ± 0.21	0.0085 ± 0.011	0.012 ± 0.012
MT	Beta-Myrcene	0.12 ± 0.11	0.024 ± 0.018	0.02 ± 0.011	0.1 ± 0.1	0.14 ± 0.16	0.0031 ± 0.0017	0.0062 ± 0.0063
MT	l-Phellandrene	0.0076 ± 0.0071	n.d.	0.0046 ± 0.003	0.0064 ± 0.0046	0.0056 ± 0.0052	0.00027 ± 0.00012	0.00027 ± 0.00014
MT	Delta 3-Carene	0.0053 ± 0.0064	0.0036 ± 0.0042	0.00026 ± 0.00015	0.0011 ± 0.00033	0.0045 ± 0.0043	0.0011 ± 0.0012	0.00044 ± 0.00022
MT	Alpha-Terpinene	0.0014 ± 0.00095	0.00024 ± 0.0002	0.0097 ± 0.0068	0.0016 ± 0.0014	0.0045 ± 0.0049	0.00052 ± 0.00032	0.00019 ± 0.000095
MT	m-Cymene	0.00041 ± 0.00038	0.000063 ± 0.000042	0.00042 ± 0.00045	0.00013 ± 0.000056	0.00047 ± 0.00025	0.00033 ± 0.00017	0.00032 ± 0.00032
MT	Limonene	0.024 ± 0.013	0.00098 ± 0.00085	0.035 ± 0.03	0.0051 ± 0.0036	0.018 ± 0.0099	0.0045 ± 0.0043	0.0016 ± 0.0013
MT	Beta-Phellandrene	0.86 ± 1.12	0.022 ± 0.019	0.036 ± 0.0094	n.d.	0.31 ± 0.21	0.0051 ± 0.0029	0.0055 ± 0.0051
MT	cis-Ocimene	n.d.	n.d.	n.d.	0.25 ± 0.21	n.d.	n.d.	n.d.
MT	trans-beta-Ocimene	0.012 ± 0.0055	0.039 ± 0.029	0.0036 ± 0.0035	0.015 ± 0.013	0.0037 ± 0.0026	0.0011 ± 0.00088	0.00093 ± 0.00061
MT	Gamma-Terpinene	0.00088 ± 0.00044	0.72 ± 0.6	0.0017 ± 0.00059	0.00062 ± 0.00046	0.0018 ± 0.0013	0.0047 ± 0.0055	0.0027 ± 0.0027
MT	p-isopropyl toluene (p-Cymene)	0.01 ± 0.011	0.00096 ± 0.0007	0.021 ± 0.014	0.005 ± 0.0038	0.013 ± 0.011	0.00097 ± 0.00064	0.00081 ± 0.0007
MT	Terpinolene	0.0043 ± 0.0019	0.0011 ± 0.00053	0.0048 ± 0.003	0.0084 ± 0.0067	0.0085 ± 0.0078	n.d.	0.00091 ± 0.00078
MT	(E)-4,8-Dimethyl-1,3,7-nonatriene	n.d.	n.d.	n.d.	0.00059 ± 0.0002	0.00054 ± 0.00033	0.049 ± 0.062	0.015 ± 0.017
MT	Alloocimene	0.0059 ± 0.0018	0.088 ± 0.066	0.0065 ± 0.0053	0.005 ± 0.0043	0.00048 ± 0.00016	0.00023 ± 0.000059	0.00015 ± 0.000071
MT	2,6-Dimethyl-1,3,5,7-octatetraene, E	n.d.	n.d.	n.d.	n.d.	0.00018 ± 0.000069	0.00018 ± 0.000059	0.00017 ± 0.00014
Total Monoterpenes		1.58 ± 1.58	0.78 ± 0.63	1.12 ± 0.82	1.15 ± 0.76	2.27 ± 1.26	0.1 ± 0.06	0.055 ± 0.062

Table 2. *(continued).*

Group	Compound	Troy Fir	Boz Pirnal Oak	Oriental Sweetgum	Cilician Fir	Uludag Fir	Ispir Oak	Vulcanic Oak
SQ	Copaene	0.00024 ± 0.00023	0.00018 ± 0.00011	0.0016 ± 0.00077	0.017 ± 0.014	0.00037 ± 0.00013	0.017 ± 0.017	0.0059 ± 0.0065
SQ	Beta-cubebene	0.00033 ± 0.00031	0.00011 ± 0.000099	0.00072 ± 0.00029	0.0015 ± 0.0014	0.00028 ± 0.00009	0.004 ± 0.0027	0.0013 ± 0.0011
SQ	Isolongifolene	0.0026 ± 0.0023	0.0017 ± 0.0024	0.0023 ± 0.0022	0.013 ± 0.011	0.0022 ± 0.00084	0.0047 ± 0.0045	0.00032 ± 0.00021
SQ	Alpha-cedrene	0.00016 ± 0.00006	0.000048 ± 0.000027	n.d.	0.00032 ± 0.00017	0.0003 ± 0.0002	0.00057 ± 0.00029	0.00049 ± 0.00038
SQ	trans-Caryophyllene	0.0041 ± 0.0036	0.00063 ± 0.00061	0.016 ± 0.0027	0.0049 ± 0.005	0.024 ± 0.029	0.043 ± 0.073	0.0079 ± 0.0084
SQ	Alpha-humulene	0.0011 ± 0.00092	0.000068 ± 0.000047	0.0011 ± 0.00041	0.0012 ± 0.0015	0.015 ± 0.0086	0.017 ± 0.0024	0.0029 ± 0.0037
SQ	Beta-farnesene	n.d.	n.d.	n.d.	0.0017 ± 0.0022	0.0019 ± 0.00042	0.0023 ± 0.00087	0.0012 ± 0.000095
SQ	Germacrene-D	0.00017 ± 0.0002	0.000091 ± 0.00006	0.0015 ± 0.0011	0.001 ± 0.00018	0.00014 ± 0.000041	0.0063 ± 0.0063	0.0014 ± 0.0012
SQ	Alpha-Bergamotene	n.d.	n.d.	n.d.	n.d.	0.00034 ± 0.000092	0.00029 ± 0.000093	n.d.
SQ	E,E-Alpha-Farnesene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.00063 ± 0.0005
SQ	Beta-selinene	0.00045 ± 0.00041	0.000082 ± 0.000075	n.d.	0.00076 ± 0.00071	0.00068 ± 0.0005	n.d.	n.d.
SQ	Alpha-muurolene	0.00026 ± 0.00026	0.00022 ± 0.00018	0.0063 ± 0.00017	0.019 ± 0.015	0.00023 ± 0.0000068	0.003 ± 0.0025	0.001014 ± 0.00073
SQ	Gamma-cadinene	0.00023 ± 0.00021	0.00017 ± 0.00016	0.005 ± 0.0044	0.012 ± 0.014	0.00046 ± 0.00019	0.0043 ± 0.0041	0.0016 ± 0.001
SQ	Alpha-cadinene	n.d.	n.d.	n.d.	0.00041 ± 0.00027	0.000065 ± 0.0000086	0.00075 ± 0.000087	0.00029 ± 0.00016
SQ	Cis-Alpha-Bisabolene	0.000085 ± 0.000049	n.d.	n.d.	0.0015 ± 0.0021	0.00062 ± 0.00014	0.00068 ± 0.00026	0.00026 ± 0.00021
Total Sesquiterpenes		0.0063 ± 0.0055	0.0022 ± 0.0023	0.018 ± 0.011	0.067 ± 0.05	0.032 ± 0.038	0.08 ± 0.097	0.02 ± 0.02
OX	2-Butanone	n.d.	0.000076 ± 0.000073	n.d.	n.d.	n.d.	n.d.	n.d.
OX	Furan, 2-methyl-	0.00043 ± 0.00032	0.00055 ± 0.00027	0.00041 ± 0.00027	0.00055 ± 0.00022	0.0027 ± 0.0014	0.0055 ± 0.0035	0.0029 ± 0.00074
OX	2-Methyl-3-buten-2-ol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
OX	Crotonaldehyde	0.0054 ± 0.0027	0.0033 ± 0.0022	0.0037 ± 0.0017	0.0055 ± 0.002	0.015 ± 0.0047	0.023 ± 0.012	0.0096 ± 0.0035
OX	Butyl aldoxime, 3-methyl-, syn-	n.d.	n.d.	n.d.	n.d.	n.d.	0.001 ± 0.00045	n.d.
OX	Isocineole	n.d.	n.d.	0.00025 ± 0.0001	0.00082 ± 0.0005	0.00048 ± 0.000089	n.d.	n.d.
OX	p-Methylanisole	0.00073 ± 0.00043	n.d.	n.d.	n.d.	0.00047 ± 0.00027	0.00023 ± 0.00011	n.d.
OX	Eucalyptol	0.17 ± 0.12	0.00074 ± 0.00052	0.017 ± 0.0098	0.027 ± 0.027	0.28 ± 0.11	0.014 ± 0.016	0.038 ± 0.026
OX	1-Octanol	0.011 ± 0.0092	0.0077 ± 0.0064	0.011 ± 0.0093	0.0029 ± 0.0011	0.0076 ± 0.0029	0.0021 ± 0.0011	0.0025 ± 0.0013
OX	Dihydromyrcenol	0.009 ± 0.0062	0.0097 ± 0.013	0.005 ± 0.0046	0.00052 ± 0.00028	0.0014 ± 0.0011	0.00085 ± 0.00011	0.0004 ± 0.00022
OX	Gamma-Terpineol	0.0088 ± 0.0075	0.009 ± 0.0029	0.03 ± 0.009	0.014 ± 0.011	0.0085 ± 0.009	0.001 ± 0.00039	n.d.
OX	L-Fenchone	0.0011 ± 0.0014	0.00019 ± 0.0002	0.00062 ± 0.00014	0.00038 ± 0.00018	0.0014 ± 0.00038	n.d.	0.00023 ± 0.00019
OX	Rosefuran	n.d.	0.00089 ± 0.00019	n.d.	n.d.	n.d.	0.00065 ± 0.00032	n.d.
OX	Tetrahydrolinalool	n.d.	n.d.	n.d.	n.d.	0.00045 ± 0.00021	n.d.	n.d.
OX	Linalool L	n.d.	0.0093 ± 0.0075	0.016 ± 0.012	0.053 ± 0.049	0.03 ± 0.023	0.066 ± 0.061	0.018 ± 0.012

Table 2. *(continued).*

Group	Compound	Troy Fir	Boz Pirnal Oak	Oriental Sweetgum	Cilician Fir	Uludag Fir	Ispir Oak	Vulcanic Oak
OX	D-Fenchyl alcohol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
OX	2-Methyl-6-methylene-1,7-octadien-3-one	0.0071 ± 0.0071	n.d.	n.d.	0.00049 ± 0.00027	0.0015 ± 0.00048	n.d.	n.d.
OX	2-tert-Butylcyclohexanone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
OX	trans-Dihydro-b-terpineol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
OX	Camphor	0.0048 ± 0.0038	0.00037 ± 0.00024	0.0011 ± 0.0011	0.0008 ± 0.001	0.096 ± 0.11	0.001 ± 0.00084	0.0012 ± 0.00064
OX	Isoborneol	0.0057 ± 0.0046	n.d.	n.d.	0.00021 ± 0.000037	0.014 ± 0.0054	0.0022 ± 0.0033	0.002 ± 0.001
OX	d-Pinocarvone	0.014 ± 0.011	0.002 ± 0.0021	0.00099 ± 0.0014	0.00057 ± 0.00047	0.0051 ± 0.0025	0.001 ± 0.00039	n.d.
OX	2-(1,1-dimethylethyl)-cyclohexanol	n.d.	0.0022 ± 0.0018	n.d.	n.d.	n.d.	n.d.	n.d.
OX	4-Terpineol	0.06 ± 0.069	n.d.	0.055 ± 0.03	0.02 ± 0.02	0.016 ± 0.021	0.0012 ± 0.00078	0.00075 ± 0.0005
OX	Alpha-Terpineol	0.27 ± 0.29	0.0061 ± 0.0044	0.021 ± 0.013	0.015 ± 0.016	0.037 ± 0.032	0.0053 ± 0.0025	0.0044 ± 0.0056
	Total Oxygenated Compounds	0.53 ± 0.44	0.029 ± 0.019	0.14 ± 0.05	0.13 ± 0.11	0.49 ± 0.2	0.091 ± 0.06	0.059 ± 0.04
OX-SQ	Methyl Eugenol	0.00019 ± 0.00019	0.00015 ± 0.000062	n.d.	0.00015 ± 0.000085	0.00013 ± 0.000049	0.00029 ± 0.00021	0.00013 ± 0.000079
OX-SQ	(-)-Spathulenol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
OX-SQ	Guaiol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Total Oxygenated Sesquiterpenes	0.00016 ± 0.00019	0.00005 ± 0.00008	n.d.	0.0001 ± 0.0001	0.00011 ± 0.00007	0.00019 ± 0.00022	0.00006 ± 0.00009

n.d.: Not detected; MT: monoterpenes; SQ: sesquiterpenes; OX: oxygenated compounds; OX-SQ: oxygenated sesquiterpenes.

Six levels of VOC solutions were prepared in methanol as the calibration standards. Thermal desorption tubes used for calibration were loaded by spiking with 1 µL of the calibration standards following the US EPA TO-17 Method (U.S. EPA, 1999). The standard spike volume was selected based on the recent studies, indicating that 1 µL spike volume does not interfere with the analytes due to solvent effect (Kim and Kim, 2012; Kim *et al.*, 2013). Then, the standard loaded tubes were run at specified conditions to calibrate the analytical system (Thermal desorber-GC-MS) (Odabasi *et al.*, 2005; Dincer *et al.*, 2006). In all cases linear fit was good with $r^2 > 0.999$.

Quality Assurance/Quality Control

Instrumental detection limits (IDL) were determined from linear extrapolation, based on the lowest standard in calibration curve and using the area of a peak having a signal/noise ratio of 3. The quantifiable VOC amounts were between 5.7 (p-cymene) and 295 pg (guaiol). Blank Tenax tubes were routinely placed in the field to determine if there was any contamination during sample handling and preparation. The method detection limit (MDL, pg) was defined as the mean blank mass plus three standard deviations. Instrumental detection limit was used for the compounds that were not detected in blanks. MDL ranged between 7.5 (trans-dihydro-b-terpineol)-1455 (crotonaldehyde) pg. Average VOC amounts in blanks were less than 5% of the amounts found in samples. Samples were blank-corrected by subtracting the average blank amount from the sample amount. MDL determined using an average sampling volume of 0.009 m^3 ranged between 0.0008 (trans-dihydro-b-terpineol) and 0.16 (crotonaldehyde) $\mu g/m^3$.

The system performance was confirmed daily by analyzing a midrange calibration standard. If the relative standard deviation from the initial calibration was < 10%, system was recalibrated. Analytical precision determined from three pairs of duplicate samples ranged between 2–5%.

Inlet concentrations of the chamber were close to blank concentrations indicating that activated carbon trap effectively removed the BVOCs from purge air. Use of the cold water circulation kept the temperature difference between the ambient air and bag within 5°C. Net photosynthesis rates during the samplings were also calculated using the leaf area, inlet and outlet CO_2 concentrations, and purge flow rate. Average rates ranged between –1110 and 27600 µmol CO_2/m^2 h, indicating that photosynthesis was the dominant mechanism rather than respiration during the samplings.

For six samples, a back-up tube was connected in series with the sample tube during sampling from the enclosure to check if there was any breakthrough. Back-up tubes contained similar BVOC quantities as the blanks indicating that the breakthrough from the sample tubes was not a problem during sampling.

Calculation of Normalized BVOC Emissions Rates

In this study, emission rates (ε, µg compound/g h) of the investigated BVOCs were determined using the measured BVOC concentrations, air flow-rates, sampling period and dry weight (or surface area) of the enclosed leaves as given

in Eq. (1) (Ortega *et al.*, 2008).

$$\varepsilon = \frac{(C_{outlet} - C_{inlet})Qt}{mt} \quad (1)$$

where, C_{outlet} and C_{inlet} are the concentrations (μg/m^3) measured at the outlet and inlet of the chamber, respectively; Q is the air flow-rate (m^3/h) pumped into the chamber; t is the sampling period (h), and m is the dry mass (g) of enclosed leaves.

Since the environmental conditions varied during samplings, all experimentally determined emission rates were normalized to standard conditions (30°C temperature and 1000 μmol/m^2 s PAR for isoprene and 30°C temperature for the remaining compounds). The temperature and light dependent algorithm by Guenther *et al.* (1993) for non-storing species was used to normalize the BVOC emissions.

Monoterpene emission rates under experimental conditions were normalized depending on the enclosure temperature as follows (Guenther *et al.*, 1993):

$$\varepsilon_{mtp} = \varepsilon_{mtp}\, \gamma_{mtp} \quad (2)$$

$$\gamma_{mtp} = \exp\left[\beta(T - T_s)\right] \quad (3)$$

where, ε_{mtp} is the monoterpene emission rate under experimental conditions, ε_{mtps} is the normalized emission rate under standard conditions (30°C), T is the enclosure temperature (K), T_s is the standard temperature (303 K), β is the empirical constant and γ_{mtp} is the correction factor. β has been determined previously from measurements of the emission rate as a function of temperature. It is typically around 0.09–0.10 for monoterpenes (Guenther *et al.*, 1993; Guenther *et al.*, 2006) and 0.17–0.25 for sesquiterpenes (Helmig *et al.*, 2006; Matsunaga *et al.*, 2011). In the present study, β was used as 0.10 for monoterpenes and oxygenated BVOCs, and 0.17 for sesquiterpenes and oxygenated sesquiterpenes since they are used as the default parameters for MEGAN model (Guenther *et al.*, 2012).

Isoprene emission rate (ε_{isos}) under standard conditions (30°C and 1000 μmol/m^2 s PAR) is determined by correcting the emission rate (ε_{iso}) at any temperature and PAR with temperature (C_T) and light (C_L) correction factors (Guenther *et al.*, 1993):

$$\varepsilon_{iso} = \varepsilon_{isos}\, \gamma_{iso} \quad (4)$$

$$\gamma_{iso} = C_L C_T \quad (5)$$

Light (C_L) and temperature (C_T) based correction factors are formulated as:

$$C_L = \frac{\alpha C_{L1} L}{\sqrt{(1 + \alpha^2 L^2}} \quad (6)$$

where, C_{L1} (1.066) and α (0.0027) are the empirical constants, L is te PAR value (μmol/m^2 s).

$$C_T = \frac{\exp C_{T1}(T - T_S)/RT_S T}{1 + \exp C_{T2}(T - T_M)/RT_S T} \quad (7)$$

where, T is the enclosure temperature (K), R is the ideal gas constant (8.314 J/K/mol), T_s is the standard temperature (303 K), T_M (314 K), C_{T1} (95000 J/mol) and C_{T2} (230000 J/mol) are the empirical constants.

A clear light dependency for several Mediterranean terpene-storing and non-storing species emitting large amounts of monoterpene emissions has been established in the literature (Loreto *et al.*, 1996; Bertin *et al.*, 1997; Staudt *et al.*, 1997; Llusia and Penuelas, 1998; Penuelas and Llusia, 1999; Llusia and Penuelas, 2000; Owen *et al.*, 2002; Keenan *et al.*, 2009; Demarcke *et al.*, 2010). In this study, the Guenther algorithm referred above was used to normalize the measured monoterpene emissions from all tree species since the recent studies have taken into account this approach (Baghi *et al.*, 2012; Matsunaga *et al.*, 2012a; Pokorska *et al.*, 2012a, b; Helmig *et al.*, 2013; Kajos *et al.*, 2013; Matsunaga *et al.*, 2013). Morever, there is not any information in the literature as to whether these endemic species are terpene-storing or non-storing.

RESULTS AND DISCUSSION

Normalized BVOC Emission Rates

Emissions for 65 analyzed BVOCs were calculated under experimental conditions and then, normalized to standard conditions of 30°C temperature and 1000 μmol/m^2 s PAR or to 30°C only (see the section *Calculation of Normalized BVOC Emissions Rates*). Table 2 summarizes the average normalized emission rates of 65 BVOC species for seven endemic tree species in Turkey.

On the basis of total emissions, Ispir Oak, Oriental Sweetgum and Cilician Fir were the highest three BVOC emitters with the total normalized emission rates of 19.4 ± 19.2, 16.3 ± 16.1 and 15.5 ± 11.4 μg/g/h, respectively while Boz Pirnal Oak had the lowest normalized emission rate of 0.84 ± 0.68 μg/g/h. Isoprene was the prominent compound for Cilician Fir, Vulcanic Oak, Ispir Oak and Oriental Sweetgum while the others were mainly monoterpene emitters (Fig. 3). Monoterpenes dominated the emissions of three species, i.e., Boz Pirnal Oak, Troy Fir, and Uludag Fir. Boz Pirnal Oak had the highest monoterpene ratio of 93% in total BVOC emissions and Uludag Fir had the highest emission rate of 2.27 ± 1.26 μg/g/h. On the other hand, sesquiterpenes were a relatively less significant BVOC group as they contributed less than 0.8% to total emissions. Oxygenated compounds had higher percentages than sesquiterpenes for all tree species and even than isoprene for Boz Pirnal Oak. Furthermore, 15 and 11% of all emissions consisted of oxygenated compounds for Troy Fir and Uludag Fir, respectively.

The ratio of monoterpenes to sesquiterpenes was different among the species. The ratio ranged from 1 to 193 for Ispir Oak and Troy Fir, respectively. The composition pattern could be classified into three types; monoterpene-rich group (Troy Fir, Boz Pirnal Oak), sesquiterpene-rich group (Vulcanic

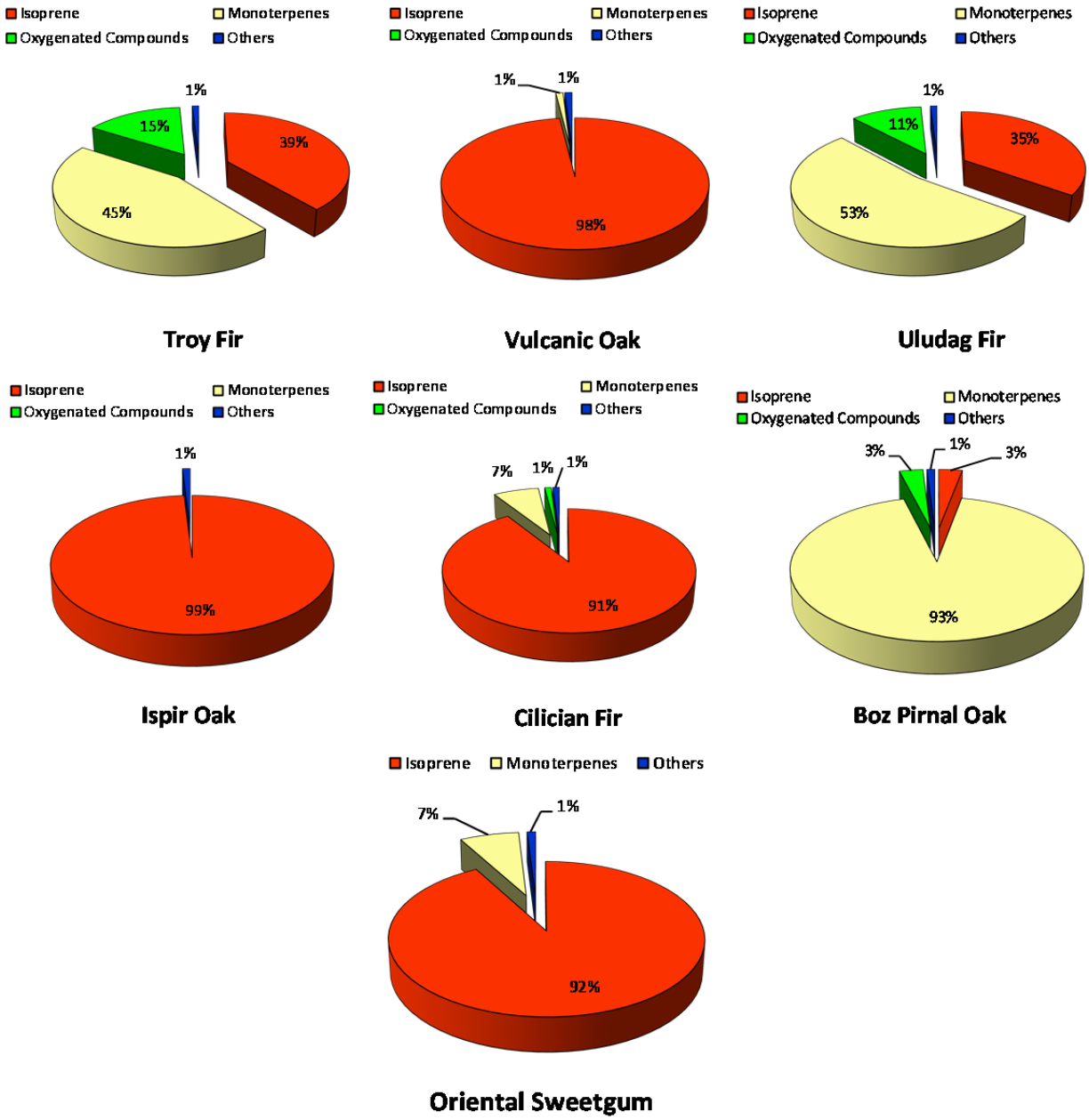

Fig. 3. Contribution of each BVOC group to total emissions.

Oak, Ispir Oak), and the intermediate group (other four species).

Characterization of BVOC Emissions

Alpha-pinene, beta-pinene, beta-myrcene and limonene are the most characteristic compounds specifying the general monoterpene emission profiles (Table 2 and Fig. 4). Limonene was emitted by all trees except by Cilician Fir, while beta-phellandrene was emitted only by Cilician Fir. Monoterpene emissions of Boz Pirnal Oak and Oriental Sweetgum mainly consisted of trans-beta-ocimene (77%) and sabinene (82%), respectively. As previously mentioned, Oriental Sweetgum is a featured tree with its unique essential oils and secretions that are used for medicinal purposes, therefore, sabinene might be a marker compound for its extracts. Even they showed lower contributions to total emissions, trans-caryophyllene, isolongifolene, alpha-humulene and copaene are the prominent sesquiterpenes (Fig. 5). As shown in Fig. 6, predominant oxygenated compounds were eucalyptol, linalool-L and alpha-terpineol. However, no linalool-L emission was detected from Troy Fir.

Fir species are known as mainly monoterpene emitters with the dominant compounds like alpha-pinene, beta-pinene, limonene and camphene, and relatively low isoprene emissions were reported in previous studies (Moukhtar *et al.*, 2006, Dominguez-Taylor *et al.*, 2007). Two of the fir species (Uludag Fir and Troy Fir) investigated in this study clearly showed a similar tendency. Monoterpenes had the highest portion with nearly 50% in total BVOC emissions for these species (Fig. 3). Pokorska *et al.* (2012b) reported

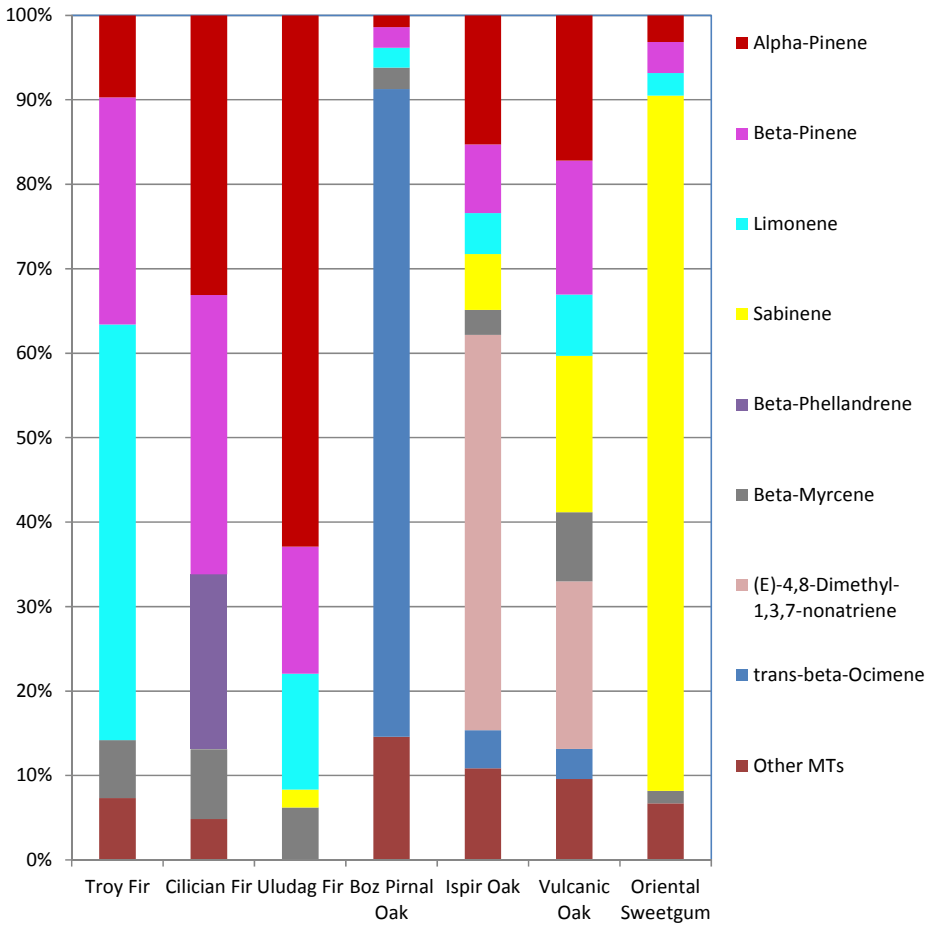

Fig. 4. Percentages of the eight most prominent monoterpenes.

that alpha-pinene, camphene, beta-pinene and limonene emissions from Silver Fir (*Abies alba*) in Belgium were in the ranges of 0.168–0.822, 0.158–1.026, 0.069–0.402 and 0.278–0.648 µg/g/h, respectively. In the present study, 0.17 and 1.42 µg/g/h of alpha-pinene, 0.86 and 0.31 µg/g/h of limonene, 0.47 and 0.34 µg/g/h of beta-pinene emissions were determined for Troy Fir and Uludag Fir, respectively. In contrast, Cilician Fir was determined as an isoprene emitter. Although it has a high isoprene ratio of 91%, it emits considerable amounts of monoterpenes as much as the other fir species. Similarly, Harrison *et al.* (2001) reported average annual isoprene and monoterpene emission rates of 18.4 ± 3.8 µg/g/h and 2.7 ± 1.1 µg/g/h, respectively for Bulgarian Fir (*Abies borisii-regis*) which is endemic to Balkans. Table 3 shows these comparisons in detail.

Oak species are strong isoprene emitters as broad-leaved trees. However, a considerable variation was observed within the reported values in the literature (see Table 3). In previous studies, researchers have commonly focused on isoprene emissions for oak species and therefore, rarely determined the emission rates for monoterpenes or any other BVOCs. Two of three studied oak species (Vulcanic Oak and Ispir Oak) exhibited the typical emitting characteristics of the genus. However, Boz Pirnal Oak was different with substantially lower isoprene emission (0.028 ± 0.026 µg/g/h). Although the monoterpene emission rate was also relatively low (0.78 ± 0.63 µg/g/h), its contribution (about 93%) to total BVOCs makes the tree a monoterpene emitter. Another oak species, Holly Oak (*Quercus ilex*) is one of the most widely investigated in previous studies (Street *et al.*, 1997; Loreto *et al.*, 1998a; Grote *et al.*, 2006) due to its prominently high monoterpene emitting potentials.

Differences in BVOC emission characteristics of the congeners in this study might be resulted from anatomical variations and/or biotope conditions. Cilician Fir had geographically different habitat conditions. It grows on lime-soils at southern latitudes while the others prefer humid and acidic soils of northern latitudes. This might affect the BVOC emission compositions. Relatively high isoprene emissions for fir species were also reported by some other researchers (Harrison *et al.*, 2001; Pokorska *et al.*, 2012b). Rasmussen (1978) conducted a detailed survey on several tree species to determine their isoprene emissions. Silver Fir and Grecian Fir (*Abies cephalonica*) were shown to emit isoprene, however, any emission rate was not reported. Presently, there is no specified parameter that could be related to these unusual emitting behaviors. However, habitat conditions, growing stages, metabolic and enzymatic processes, unidentified stress factors or genetic constitutions might be effective (Street *et al.*, 1997; Fall, 1999; Kim *et al.*, 2005; Singh *et al.*, 2007; Joó *et al.*, 2010). On the other hand, as an evergreen tree, Boz Pirnal Oak is anatomically

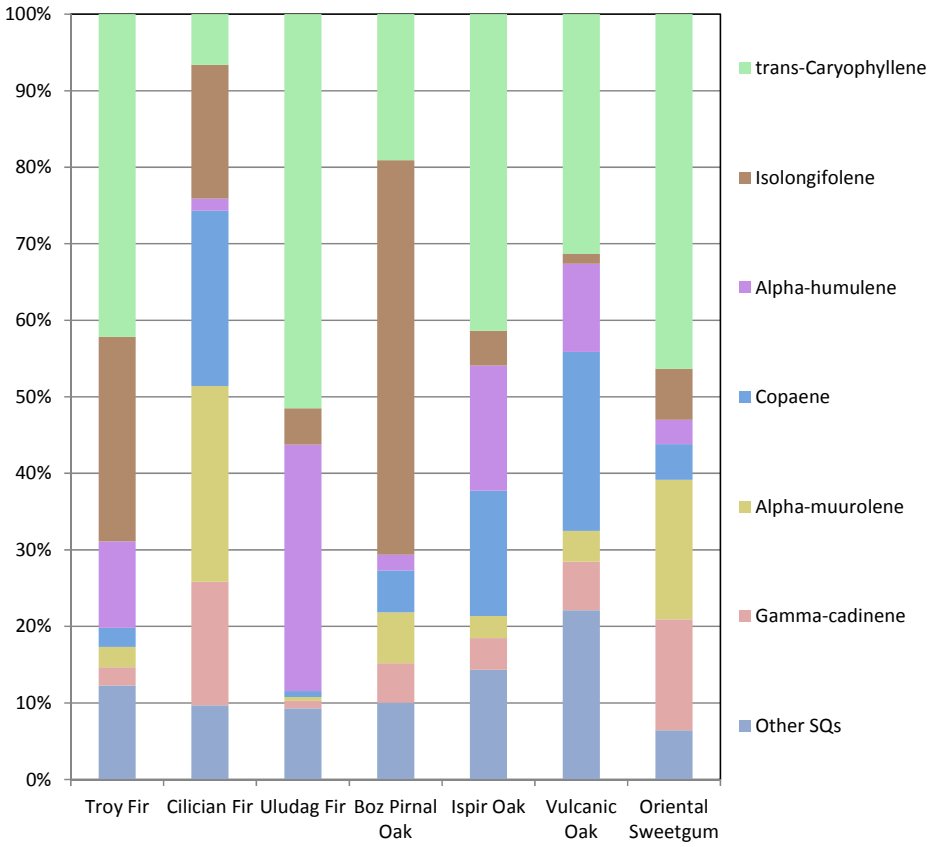

Fig. 5. Percentages of the six most prominent sesquiterpenes.

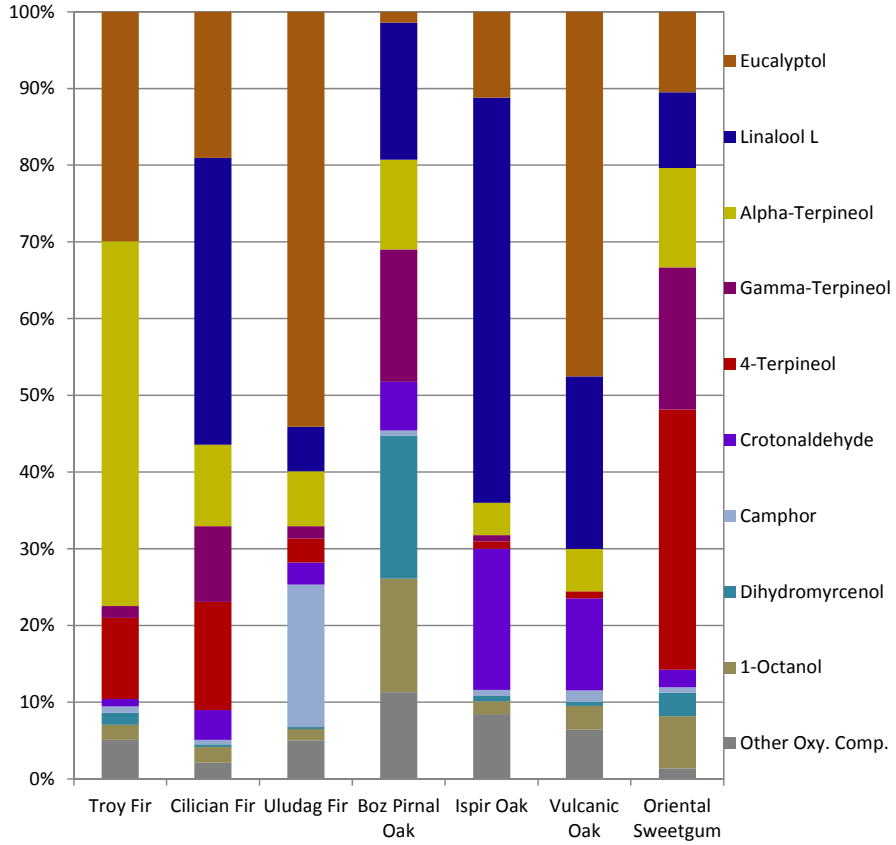

Fig. 6. Percentages of the nine most prominent oxygenated compounds.

Table 3. Comparison of the normalized emission rates previously reported in the literature (at 1000 μmol/m^2/s and 30°C).

Common Name	Genus/Species	Distribution Region	Emission Factor (μg/g/h)			Number of Samples	Reference
			Isoprene	Monoterpenes	Sesquiterpenes		
Silver Fir	*Abies alba*	Europe	< 0.1	0.63	n.r.	62	(Moukhtar *et al.*, 2006)
			1	1	0.1	n.r.	(Steinbrecher *et al.*, 2009)
			4.6–27	0.26–2.85[a]		18	(Pokorska *et al.*, 2012b)
Sacred Fir	*Abies religiosa*	Mexico	n.d.	6.066	n.r.	12	(Dominguez-Taylor *et al.*, 2007)
Bulgarian Fir	*Abies borisii-regis*	Balkans	18.4 ± 3.8	2.7 ± 1.1	n.r.	n.r.	(Harrison *et al.*, 2001)
Balsam Fir	*Abies balsamea*	intercontinental	n.r.	3.40 ± 2.60	< 0.01	5	(Ortega *et al.*, 2008)
Grand Fir	*Abies grandis*	N.W. of the USA	n.r.	0.36 ± 0.27	0.01 ± 0.01	15	This study
Greek Fir	*Abies cephalonica*	Greece	n.r.	0.63	0.1	n.r.	(Steinbrecher *et al.*, 2009)
Troy Fir	*Abies equi-trojani*	Turkey	1.34 ± 1.11	1.58 ± 1.58	0.0063 ± 0.0055	6	This study
Cilician Fir	*Abies cilic.* subsp. *isaur.*	Turkey	14.1 ± 10.5	1.15 ± 0.76	0.067 ± 0.050	6	This study
Uludag Fir	*Abies nord.* subsp. *born.*	Turkey	1.50 ± 1.39	2.27 ± 1.26	0.032 ± 0.038	6	This study
Holly Oak	*Quercus ilex*	Mediteranean Region	0.1	43	0.1	n.r.	(Steinbrecher *et al.*, 2009)
			0.007 ± 0.011	12.0 ± 12.7	n.r.	n.r.	(Owen *et al.*, 1997)
			n.r.	21.7 ± 2.00	n.r.	n.r.	(Bertin *et al.*, 1997)
			n.r.	21.1 ± 19.8	n.r.	115	(Sabillon and Cremades, 2001)
			n.r	17.5 ± 10.2	n.r.	7 to 15	(Kesselmeier *et al.*, 1998)
			6.14 ± 4.95	0.0094 ± 0.0036	0.0050 ± 0.0030	6	(Elbir *et al.*, 2013)
Sessile Oak	*Quercus petraea*	Europe and Anatolia	43	0.1	0.1	n.r.	(Steinbrecher *et al.*, 2009)
			< 0.17–7.05	n.r.	n.r.	n.r.	(Steinbrecher *et al.*, 1997)
			0.61	0.12	n.r.	2	(Konig *et al.*, 1995)
Pendunculate Oak	*Quercus robur*	Europe, Anatolia, Caucasus and N. Africa	58.28	0.68	n.r	n.r.	(Perez-Rial *et al.*, 2009)
			70	1	0.1	n.r.	(Steinbrecher *et al.*, 2009)
			61	0.23	n.r	77[b]	(Pokorska *et al.*, 2012a)
Hungarian Oak	*Quercus frainetto*	S.E. of Europe, Balkans and Turkey	85	n.r.	0.1	n.r.	(Steinbrecher *et al.*, 2009)
			133.95	n.r.	n.r.	n.r.	(Steinbrecher *et al.*, 1997)
Canyon Live Oak	*Quercus chrysolepis*	California, Mexico	48	n.r.	n.r.	10	(Geron *et al.*, 2001)
Valley Oak	*Quercus lobata*	California	86	n.r.	n.r.	14	(Geron *et al.*, 2001)
Kermes Oak	*Quercus coccifera*	Mediteranean Region and N. of Africa	n.d.	0.0009	n.r.	1	(Dasdemir *et al.*, 2012)
-	*Quercus rotundifolia*	South Europe, Algeria, North Africa	0.2	14.6	0.1	n.r.	(Steinbrecher *et al.*, 2009)
Northern Red Oak	*Quercus rubra*	North America	35	0.1	0.1	n.r.	(Steinbrecher *et al.*, 2009)
Downy Oak	*Quercus pubescens*	South Europe and Southwest Asia	70	0.3	0.1	n.r.	(Steinbrecher *et al.*, 2009)

Table 3. *(continued)*.

Common Name	Genus/Species	Distribution Region	Emission Factor (μg g/h)			Number of Samples	Reference
			Isoprene	Monoterpenes	Sesquiterpenes		
Vulcanic Oak	*Quercus vulcanica*	Turkey	9.79 ± 7.57	0.055 ± 0.062	0.020 ± 0.020	6	
Ispir Oak	*Quercus macr.* subsp. *syspir.*	Turkey	19.2 ± 19.0	0.10 ± 0.060	0.080 ± 0.097	6	This study
Boz Pirnal Oak	*Quercus aucheri*	Turkey	0.028 ± 0.026	0.78 ± 0.63	0.0022 ± 0.0023	6	
American Sweetgum	*Liquidambar styraciflua*	North and Central America	29.0 ± 16.5	n.r.	n.r.	15–17	(Harley *et al.*, 1996)
			68	n.r.	n.r.	11	(Geron *et al.*, 2001)
Oriental Sweetgum	*Liquidambar orientalis*	Turkey	15.0 ± 15.2	1.12 ± 0.82	0.018 ± 0.011	6	This study

n.d.: not detected, n.r.: not reported.
[a] The reported value refers to sum of monoterpenes and sesquiterpenes.
[b] Sum of the collected number of samples for studied two tree species (Q. robur and F. excelsior).

dissimilar to the other two studied deciduous oaks. It is a small shrub-like tree, reaching a maximum height of 5–6 meters and prefers low altitudes and high temperature zones. Therefore, emissions of Boz Pirnal Oak did not show similarities with Vulcanic Oak and Ispir Oak. Another oak species, Kermes Oak (*Quercus coccifera*) having similar characteristics with Boz Pirnal Oak, was also reported as a low BVOC emitter (Dasdemir *et al.*, 2012). Likewise, Vulcanic Oak and Ispir Oak were also physically comparable with some massive oaks previously investigated in the literature such as Pedunculate Oak (*Quercus robur*) and Sessile Oak (*Quercus petraea*) with their typically high-isoprene and low-monoterpene emission patterns (see Table 3). Furthermore, monoterpene, sesquiterpene and oxygenated compound compositions of these species were mainly consist of the same predominant compounds as illustrated in Figs. 4, 5 and 6.

Based on their studies on several oak species, Loreto *et al.* (1998b) and Loreto (2002) have concluded that (i) oaks grown in the western hemisphere emit mainly isoprene; (ii) monoterpene emission is specific to evergreen oaks of the Mediterranean environment; (iii) another group of Mediterranean oaks does not emit isoprenoids in substantial amounts; and (iv) the differences in emission profiles generally matches the taxonomical classification of oaks based on anatomical or molecular markers. The emission profiles for different oak species observed in the present study were in close agreement with these findings.

CONCLUSIONS

BVOC emission rates from seven endemic tree species in Turkey were determined using a specific dynamic branch enclosure system. Five of seven species (Uludag Fir, Troy Fir, Ispir Oak, Vulcanic Oak and Oriental Sweetgum) showed the typical emitting behaviors of their genus. As commonly reported in the literature, isoprene and monoterpenes were predominant compounds for all species. The highest isoprene and monoterpene amounts were emitted by Ispir Oak and Uludag Fir with the normalized emission rates of 19.2 ± 19.0 and 2.27 ± 1.26 μg/g/h, respectively. Oxygenated compounds were the third most prominent group and sesquiterpenes had relatively lower portions with a maximum value of 0.080 ± 0.097 μg/g/h for Ispir Oak contributing 0.34% to its total normalized BVOC emissions. Cilician Fir and Boz Pirnal Oak had different emission compositions, similar to those that were also reported by several previous studies. It was also reported that the values determined even for same species in different studies varied substantially.

BVOC emissions of endemic tree species in Turkey were characterized for the first time in the present study. These specific emission rates could be utilized in the future BVOC inventories and air quality modeling studies.

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